

Supporting Information

Iodobenzene-Catalyzed α -Acetoxylation of Ketones. In Situ Generation of Hypervalent (Diacyloxyiodo)benzenes Using *m*-Chloroperbenzoic Acid

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Scheme S1. Attempted Deuteration of Acetophenone in the Absence of $\text{BF}_3\text{-Et}_2\text{O}$

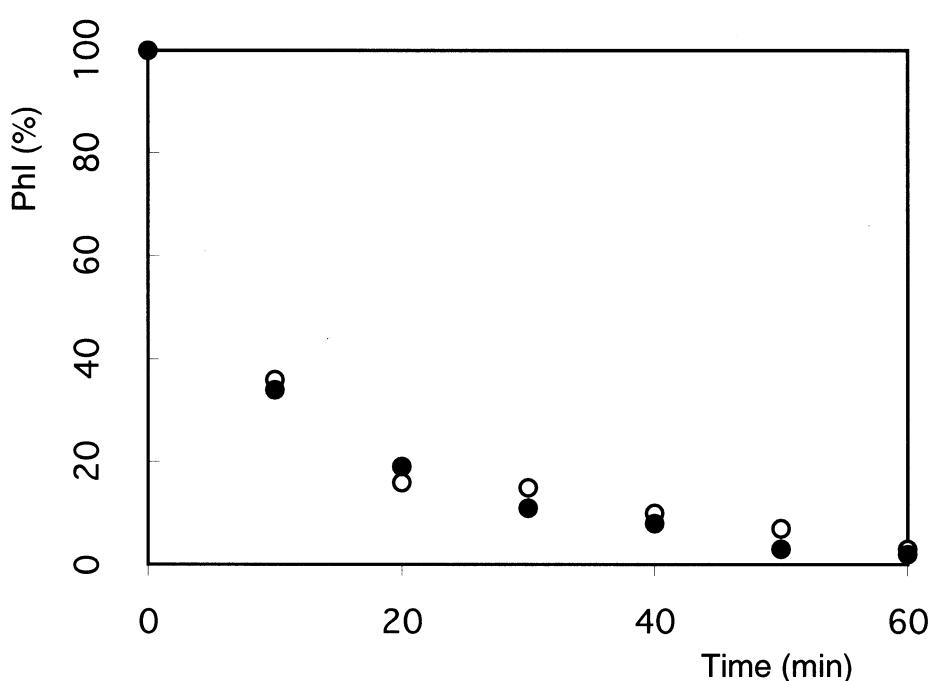
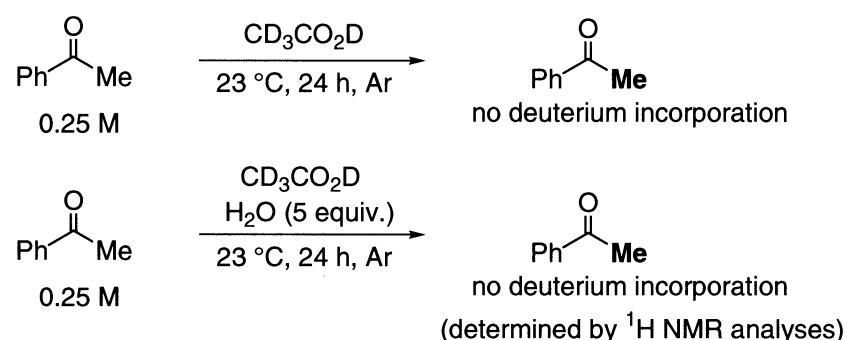


Figure S1. Time courses for oxidation of iodobenzene with *m*-CPBA in the absence of $\text{BF}_3\text{-Et}_2\text{O}$ (determined by ^1H NMR analyses). Reaction conditions: iodobenzene (0.024 M) in $\text{CD}_3\text{CO}_2\text{D}$ and *m*-CPBA (10 equiv) at 23°C under argon. (a) (\bigcirc) without D_2O , and (b) (\bullet) with D_2O (50 equiv).

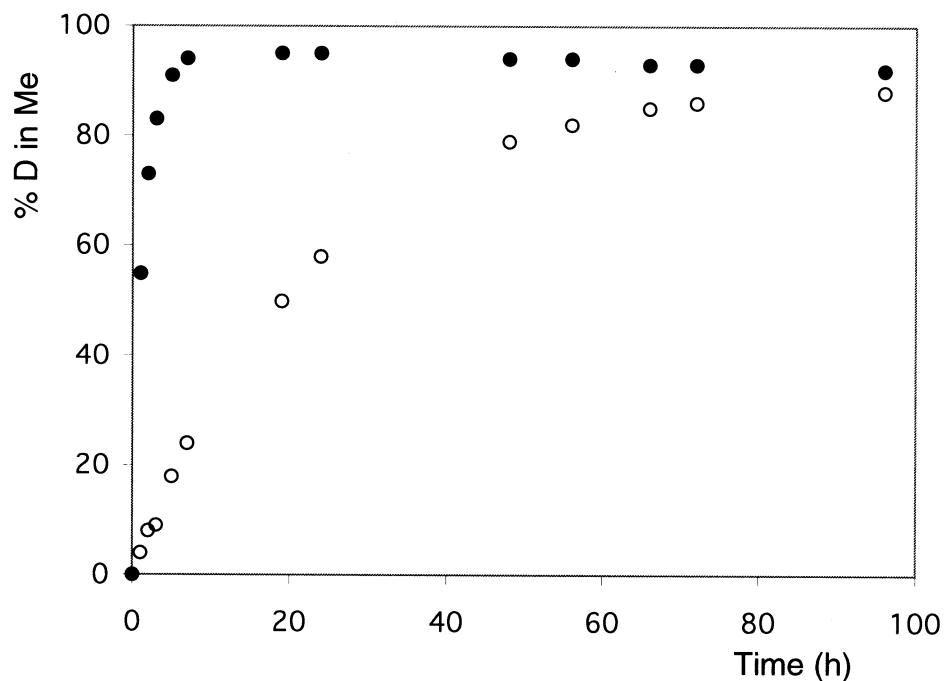


Figure S2. Time courses for the deuteration of acetophenone in the presence of $\text{BF}_3\text{-Et}_2\text{O}$ (determined by ^1H NMR analyses). Reaction conditions: acetophenone (0.25 M) in $\text{CD}_3\text{CO}_2\text{D}$, $\text{BF}_3\text{-Et}_2\text{O}$ (3 equiv) at 23 °C under argon. (a) (●) without D_2O , and (b) (○) with D_2O (5 equiv).

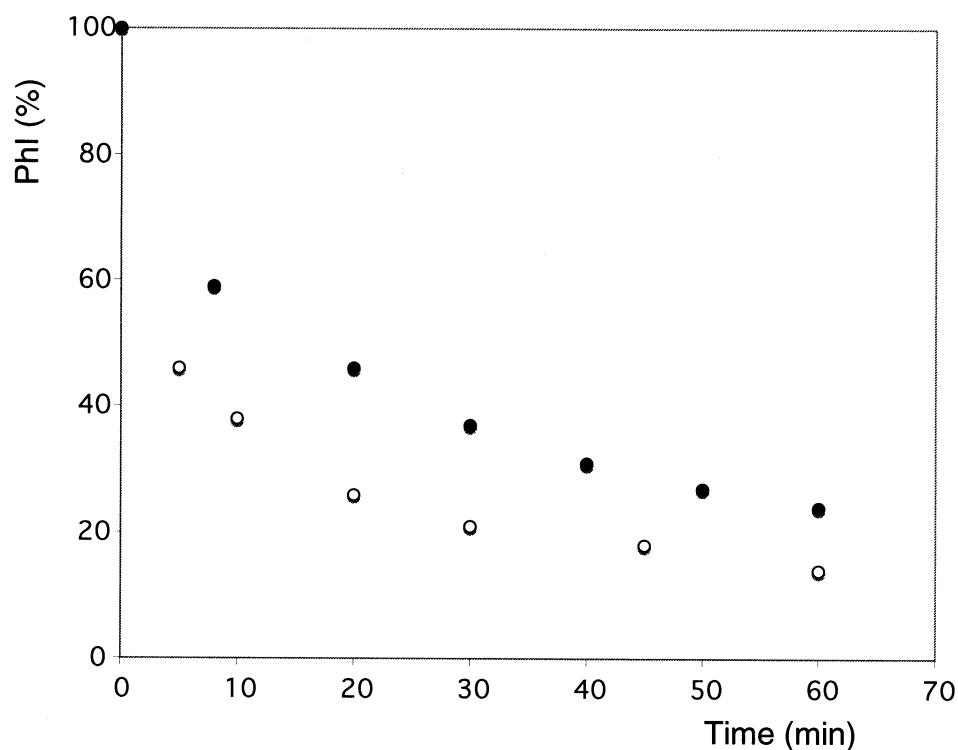


Figure S3. Time courses for oxidation of iodobenzene with *m*-CPBA (determined by ^1H NMR analyses). Reaction conditions: iodobenzene (0.25 M) in $\text{CD}_3\text{CO}_2\text{D}$, *m*-CPBA (1 equiv), and $\text{BF}_3\text{-Et}_2\text{O}$ (1 equiv) at 25 °C under argon. (a) (○) without D_2O , and (b) (●) with D_2O (5 equiv).

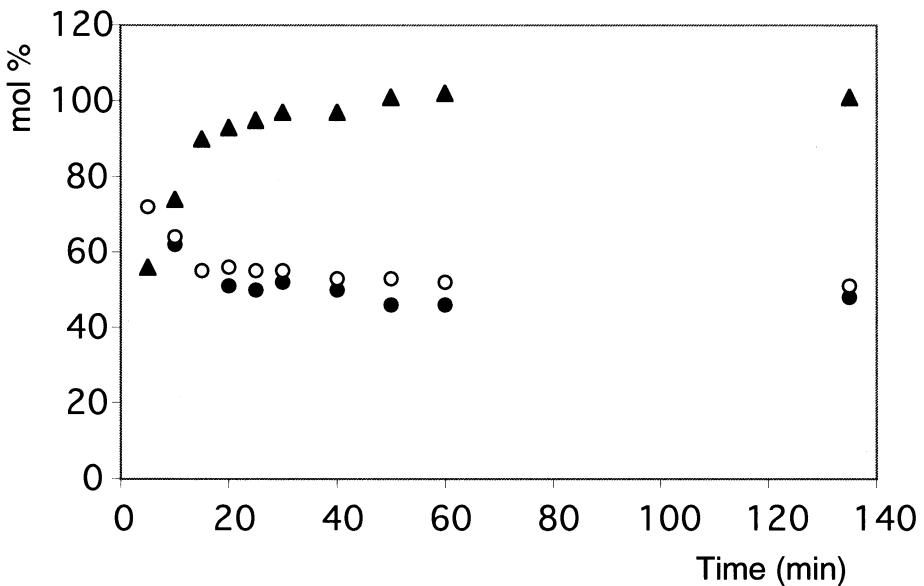


Figure S4. Ligand exchange between PhI(OAc)₂ and PhI(OCO-*m*-ClC₆H₄)₂ (determined by ¹H NMR analyses). Conditions: PhI(OAc)₂ and PhI(OCO-*m*-ClC₆H₄)₂ (each 6 mM) in CDCl₃ at 22 °C. (○) PhI(OAc)₂, (●) PhI(OCO-*m*-ClC₆H₄)₂, and (▲) PhI(OAc)OCO-*m*-ClC₆H₄.

Stoichiometric Oxidation of Acetophenone

